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Synthesis and Characterization of Soluble Oligo (9,10-Bisalkynylanthrylene)s

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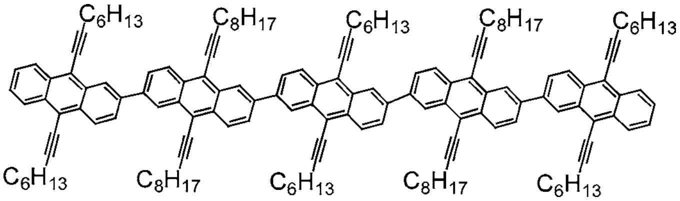
ABSTRACT



Soluble oligo(9,10-bialkynylanthrylene)s up to pentamers were synthesized by means of the Suzuki coupling reaction. A solution processed thin film field-effect transistor from pentamer OA-5b shows a charge carrier mobility of 2.95 × 10^{-3} cm^2/V·s.

Conjugated molecules are of great interest owing to their various applications in organic electronics and optoelectronics.[1,2] In general, the intermolecular packing mode in solid state is as important as molecular structure in management of the bulk properties. For instance, intermolecular close packing usually favors charge carrier transport, but not light emission.[3] Accordingly, tailoring molecular structure to modulate optical and electronic properties of conjugated materials has remained a hot topic.

Solution soluble conjugated polymers and oligomers are most promising materials in view of applications in less expensive and flexible optoelectronic devices.[2a] Of those the materials with high charge carrier mobility have recently attracted particular attention, but mainly focus on thiophene derivatives.[4] In this type of materials, molecules should densely stack in solid state to induce strong intermolecular electronic interaction. Therefore, the alkyl substituents should preferably locate in the plane of aromatic unit and, meanwhile, have no significant effect on dihedral angle between repeating units.[2a]

Monodisperse conjugated oligomers have attracted particular attention in recent years because they can not only serve as the model compounds for establishment of structure−property relationship but also be used for fabrication of high-performance devices due to well-defined structures and properties as well as morphology.[1,2] Anthracene is one of the most important fused aromatics with charge carrier mobility up to 3 cm^2/V·s in single crystals at 300 K.[5] A number of its derivatives have been reported.[6−10] However, most of these compounds are small molecular light emitters

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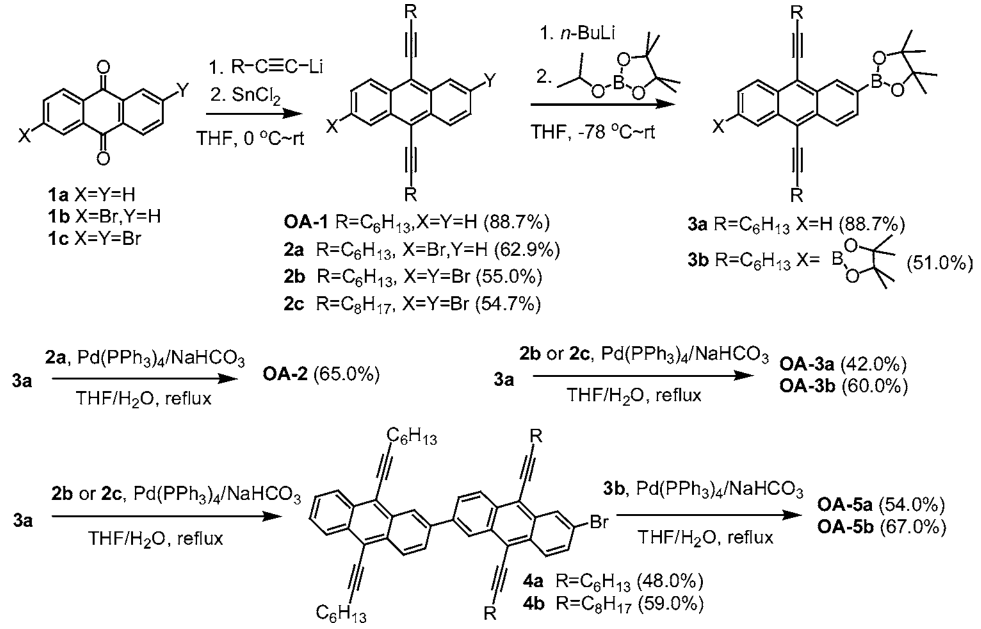
Scheme 1. Synthesis of **OAs**



for organic light-emitting diodes, and only a few anthracene-based oligomers and polymers have been reported.[11−16] Müllen et al. synthesized soluble oligo (9,10-anthrylene)s up to heptamer, in which a dihedral angle up to 82° between neighboring anthracene units due to the strong steric hindrance significantly limited interunit conjugation.[11] Recently, Ito et al. reported bi(2,6-anthrylene) and ter(2,6-anthrylene) that can be used to fabricate thin film transistors with mobility up to 0.18 cm^2/V•s via vacuum deposition.[12] In the current work, the first series of soluble oligo(2,6-anthrylene)s (**OAs**) up to pentamer were synthesized by means of a Suzuki cross-coupling reaction through introduction of a pair of alkynyl chains into the 9,10-positions of the anthracene unit (Figure 1). Since the 9,10-carbon atoms are sp^2 hybridized, these flexible chains should locate in the plane of anthracene unit. Therefore, the **OAs** should prefer intermolecular close packing for strong intermolecular electronic interactions in the solid state.[17]

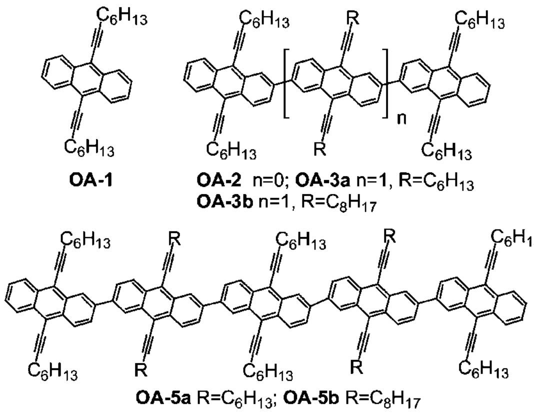


Figure 1. Structures of **OAs**.

The compounds **1b** and **1c** were synthesized via Sandmeyer reaction of 2-aminoanthraquinone and 2,6-diaminoanthraquinone, respectively.[12,18] Synthesis of the **OAs** is depicted in Scheme 1. Addition of alkynyllithium to the compounds **1a**−**c** followed by deoxygenation with stannous chloride afforded dialkynyl substituted anthracene derivatives **OA-1** and **2a**−**c** in a yield of 54−89%.[19] Boronic reagents **3a** and **3b** were synthesized through treating **2a** and **2b** with *n*-BuLi followed with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-

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Table 1. Spectroscopic and Electrochemical Properties of **OAs**

compd	$\lambda_{\mathrm{abs}}^{\mathrm{sol}\ a}$ (nm)	$\lambda_{\mathrm{PL}}^{\mathrm{sol}\ a}$ (nm)	$\lambda_{\mathrm{abs}}^{\mathrm{film}\ b}$ (nm)	HOMO	LUMO	$\Delta E_{\mathrm{g}}^{\mathrm{elec}}$ (eV)	$\Delta E_{\mathrm{g}}^{\mathrm{abs}}$ (eV)
OA-1	387, 409, 434	443, 467		−5.45	−2.85	2.60	2.79
OA-2	399, 424, 453	495	406, 435, 466	−5.36	−2.93	2.43	2.64
OA-3a	425, 443, 471	504	437, 463, 495	−5.34	−2.98	2.36	2.50
OA-3b	425, 443, 469	503	462, 496	−5.34	−2.99	2.35	2.52
OA-5a	425, 448, 483	513		−5.29	−2.98	2.31	2.41
OA-5b	425, 448, 483	514	474, 513	−5.28	−2.99	2.29	2.43

[a] Measured in chloroform with a concentration of 10^{-5} M. [b] Films were spin-coated from chloroform solution with a concentration of 8 mg/mL at 1000 rpm for **OA-2** and **OA-3a** and 6 mg/mL at 600 rpm for **OA-3b** and **OA-5b**.

dioxaborolane. The Suzuki coupling reactions were carried out in a typical condition to afford **OA-2** to **OA-5** in a yield of 42−67%. Structures of the **OAs** were verified by NMR, elemental analysis, mass spectroscopy and gel permeation chromatography (GPC).

The oligomers **OA-1** and **OA-2** are highly soluble in common organic solvents, such as chloroform, tetrahydrofuran (THF) and toluene. However, the solubility of **OAs** dramatically decreases with increasing chain length. With octynyl as the substituent, **OA-5a** is almost insoluble in any organic solvents at room temperature. This behavior is quite different from oligofluorenes; in which pentyl is long enough to endow the oligomers good solubility even the number of repeat unit is up to 16.[20] Interestingly, exchanging the octylnyl with decynyl in some repeat units can significantly enhance the solubility of **OA-3** and **OA-5**. The compound **OA-5b** has enough solubility in chloroform for fabrication of films with spin coating.

The single crystal of **OA-1** obtained from recrystallization was analyzed by means of single-crystal X-ray diffraction. As shown in Figure 2, consistent to our anticipation, the anthracene unit is planar with one pair of alkynyl chains locating in the plane. This characteristic is favorable for intermolecular close packing for **OAs**, therefore to endow good charge carrier transport in solid state.

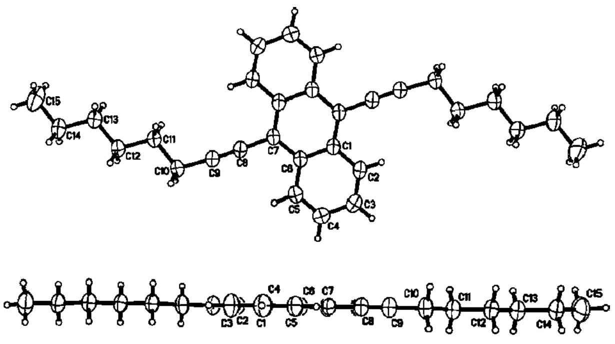

Figure 2. X-ray crystal structure of **OA-1**: top view (top) and side view (bottom).

The solution absorption and emission spectra of **OAs** were recorded in chloroform with the concentration of 10^{-5} M. The peak positions of absorption and photoluminescence spectra are summarized in Table 1. As shown in Figure 3a, in contrast to oligo(9,10-anthrylene)s,[11] the absorption band of **OAs** at the long wavelength is well-resolved and significantly red shifts with increasing molecular length. The absorption maximum red shifts from 434 nm of **OA-1** to 453 nm of **OA-2**, 469 nm of **OA-3b** and 483 nm of **OA-5b**,

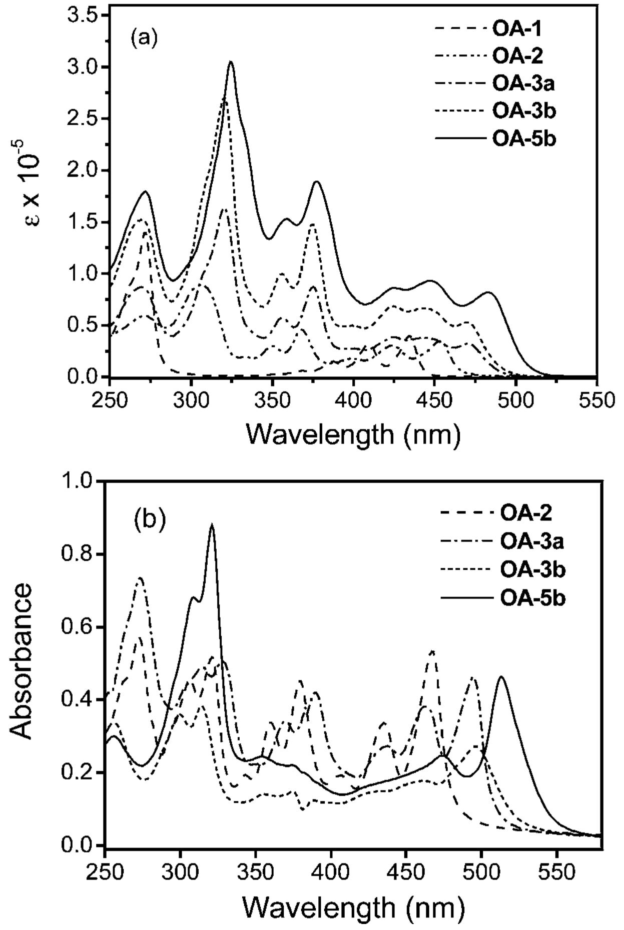

Figure 3. UV−vis absorption spectra of **OAs** in chloroform solution with the concentration of 10^{-5}M (a), and in film state (b).

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indicative of good conjugation between repeat units. The emission maximum follows the same trend and red shifts from 443 nm of **OA-1** to 514 nm of **OA-5b**. The length of alkynyl chain has no effect on positions of both absorption and photoluminescence peaks. The cyclic voltammetry of **OA**s in methylene chloride was performed in a standard three-electrode cell with the redox potentials calibrated with ferrocene. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels estimated from oxidation and reduction on-set along with the HOMO−LUMO energy gap are listed in Table 1. While the LUMO level is almost independent of the length of **OAs**, the HOMO level increases from −5.45 eV of **OA-1** to −5.28 eV of **OA-5b**. Accordingly, the HOMO−LUMO gap decreases from 2.60 eV of **OA-1** to 2.29 eV of **OA-5b**. The energy gap estimated from absorption edge decreases in the same trend with increasing the molecular length, as seen in Table 1. The film absorption spectra of **OAs** on clean silica wafer are shown in Figure 3b. In comparison to solution absorption spectra, a red shift up to 30 nm was observed. Meanwhile, in contrast to strong bluish green to yellow photoluminescence in solutions, no photoluminescence was observed in film state. These indicate strong intermolecular interaction in film state.

To test the potential of the **OAs** as the organic semiconductors, a thin film field-effect transistor of **OA-5b** with a top-contact geometry was fabricated on heavily doped silicon/SiO_2 (150 nm) substrate treated with octadecyltrichlorosilane monolayer. The **OA-5b** layer was spin-cast from chloroform solution with a concentration of 6 mg/mL and a spin rate of 750 rpm. In contrast to 6,13-bisoctynylpentacene that showed no field effect in a similar device structure,[17b] a field-effect mobility of 2.95×10^{-3} $cm^2/V{\cdot}s$ calculated from saturation region was obtained. Further study including optimizing chemical structures and device fabrication conditions is underway.

In summary, we have reported the synthesis and characterizations of soluble oligo(2,6-anthrylene)s with up to five repeating units. The oligomers have the potential to be solution processible organic semiconductors with high charge carrier mobility.

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Supporting Information Available: Experimental procedures, characterizations for all compounds, and single-crystal X-ray diffraction data of **OA-1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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